COMPRESSED LIQUID DENSITIES AND SATURATED LIQUID DENSITIES OF HFC-365mfc[1]

Bobbo Sergio[2,3], Scattolini Mauro[2], Fedele Laura[2], Camporese Roberto[2]

---

[2] National Research Council; Institute of Building Technologies – Division of Padova, Corso Stati Uniti 4, I-35127 Padua; Italy.

[3] Corresponding author: Tel.+39.049.8295736; Fax +39.049.8295728; email: sergio.bobbo@itc.cnr.it

Abstract

1,1,1,3,3-pentafluorobutane (HFC-365mfc) is currently proposed as a substitute for CFCs in several applications. Experimental data on this fluid are still not sufficient to describe accurately its thermodynamic behaviour. Liquid density is one of the most important properties required to develop precise equations of state. At the state of the art, data of compressed and saturated liquid density are lacking. In this paper density in liquid phase was measured along 8 isotherms ranging from 283.15 K to 343.06 K at pressures up to 25 MPa. The paper presents also correlations for the compressed liquid by means of a Tait equation and the saturated liquid density.

1. Introduction

Refrigeration engineering is focused on the research for new, more effective and ozone-safe substances, such as Hydrofluorocarbons (HFCs) In order to select efficient and environmentally acceptable substitutes for Chloro-Fluoro-Carbons (CFC), not only in the field of refrigeration but also in the insulation industry, there is an increasing need of new thermophysical data. These experimental data are furthermore essential in the screening phase to compare the efficiencies between different compounds.

The HFC-365mfc, a fluorinated derivative of butane, is one of the fluids considered as possible substitutes for CFCs in several applications, especially as a blowing agent in rigid insulation.

To obtain accurate volumetric properties (PVT), we used a synthetic open flow method based on a vibrating tube densimeter. The compressed liquid density has been measured in the temperature range between 283 K and 343 K with pressure up to 25 MPa. The temperature is measured with an estimated accuracy of ± 0.02 K and the pressure is accurate to within ± 2 kPa. The maximum uncertainties on the measured densities ρ is estimated to be ± 1 kg·m^{-3}.

From the knowledge of the temperature dependence of the vapour pressure, saturated liquid densities have been obtained by extrapolating isothermal compressed liquid density data up to the liquid saturated pressure.

A second objective of the present work is to correlate the experimental $P\rho T$ data for both the compressed liquid (by means of a Tait equation) and the saturated liquid density. A comparison with the existing literature data has been performed on the base of the correlations.

2. Experimental section

2.1 Principle and apparatus

The experimental set-up used in the present work is shown schematically in Figures 1 and 2. Details of the experimental VTD apparatus and measurement principles are given in previous papers [1]. The measurement principle is the determination of the vibrating period (π) of an hollow resonating tube filled with the fluid to be studied, as a function of pressure P and temperature T. Knowing the parameters of the tube, through a calibration equation,

periods can be converted into densities.

The current method is designed for isothermal runs for both measurements and vibrating tube calibration.

The main part of the apparatus is the vibrating densimeter cell DMA 512 Type (Anton Paar, Graz, Austria). The vibrating tube is fitted with a special loading circuit allowing feeding of pure compound and pressure measurements (PG). Pressure increases or decreases are obtained by operating a manual piston pump (MPP). Pressure is measured through a differential pressure gauge (Druck DPI 145, 35 MPa FS) with a maximum error of ± 20 kPa.

The experimental temperature is achieved and maintained with a stability within ±0.003 K by circulating water coming from an external thermostatic bath. Temperature in the vibrating tube cell is measured by a calibrated PT 100 Ω resistance thermometer with an estimated uncertainty within ±0.02 K. A thermal regulator maintains a fine local temperature regulation around the inlet tubes by means of an electrical heating resistance (HR) fed by a variable transformer: this ensures the temperature and density uniformity inside of the vibrating tube.

The densimeter with the measurement circuit are placed in an air thermostatic bath to keep an ambient temperature of 298.15 ± 0.05 K.

A dedicated software, developed in LabView 5.1.1 environment, allows the continuous acquisition, visualization and elaboration of the main experimental parameters (period, temperatures and pressure). An equation of state for the calibration fluid and a proper calibration equation (2) are also implemented into the software to allow the on line calculation of the experimental density.
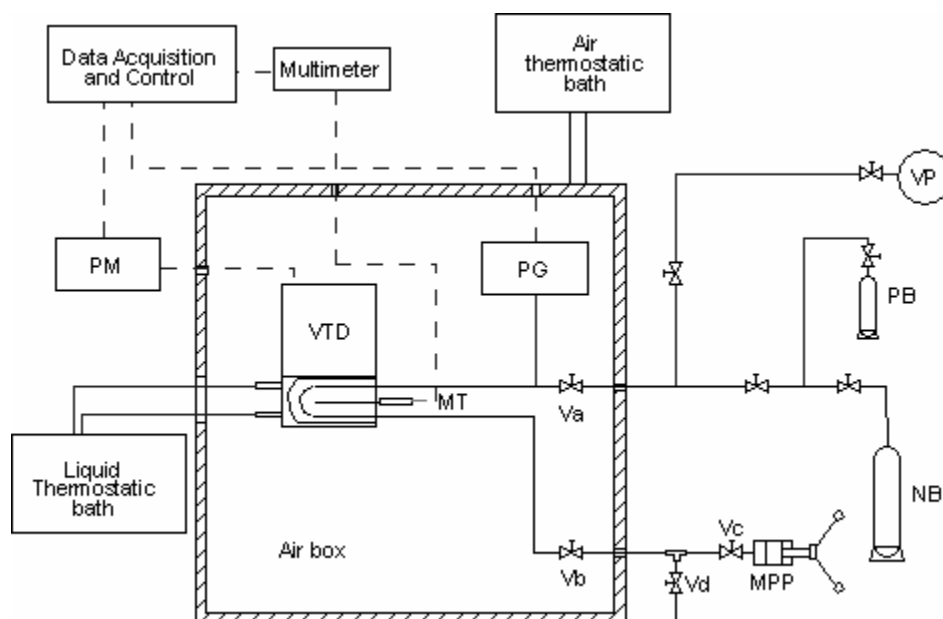
Figure 1. Density measurements apparatus scheme. MPP: manual piston pump, MT: temperature measurements sensor, NB: nitrogen bottle, PB: pure refrigerant bottle, PG: pressure gauge, V_a, V_b, V_c, V_d: on-off valves, VP: vacuum pump, VTD: vibrating tube densimeter.
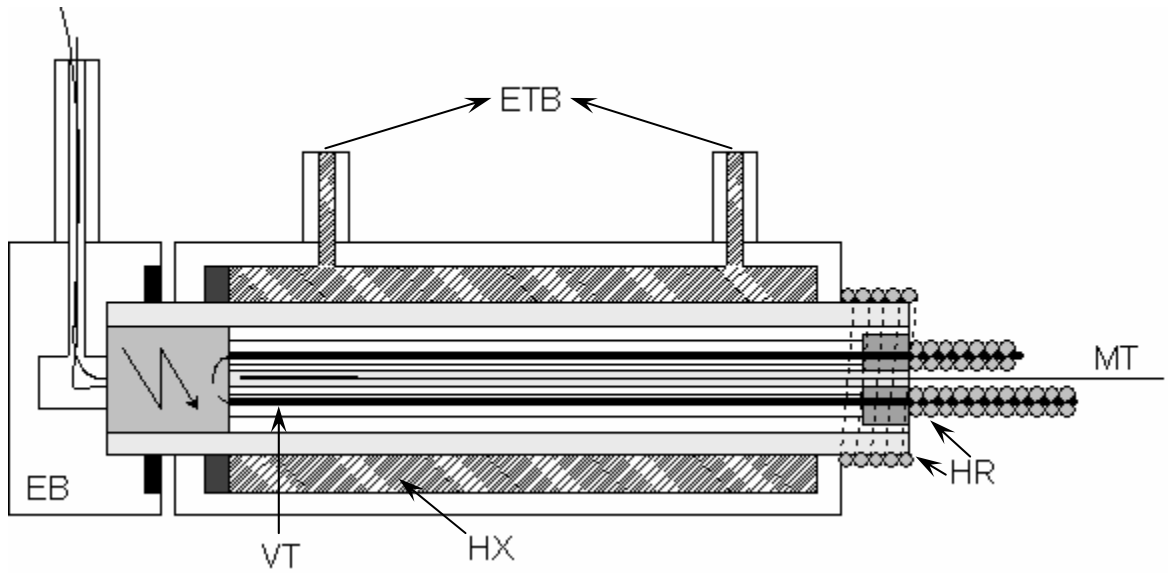
Figure 2. Measurement cell section. EB: electric box, ETB: external thermostatic box, HR: heating resistance, MT: temperature measurements sensor, VT: vibrating tube, HX: heat exchanger.

2.2 Procedure

After a careful evacuation, the circuit is filled with the liquid and the valve V_a is closed. The liquid phase is pressurized at the desired maximum pressure (25 MPa) by the manual piston pump (MPP) (RUSKA T1200V). After the temperature stabilization, valve V_c is closed, valve V_d is open and a controlled bleeding is created through valve V_b. In such a way, a small pressure drop occurs inside the vibrating tube densimeter cell (10 kPa/s). Pressures and periods are continuously recorded, till a discontinuity is observed revealing the first vapour bubble appearance. At this point, the liquid-density isotherm is completed.

The following relation is used to evaluate the density ρ of the sample fluid at a given temperature from the period of oscillation π of the vibrating tube and the pressure P:

$$\pi^2 = A \cdot \rho + B \tag{1}$$

A and B are considered as apparatus constants and they must be determined from calibration measurements. The behaviour of the vibrating tube is actually dependent on temperature, which influences the thermal expansion coefficient and the elastic constant of the vibrating tube, and pressure, that influences the elastic response.

At isothermal conditions the constant B depends only on the oscillation period under vacuum, while the constant A is dependent also on pressure. The actual calibration curve, applied at constant temperature, is the following:

$$\pi^2 = \left(a \cdot P^2 + b \cdot P + c\right) \cdot \rho + B \tag{2}$$

The coefficients *a*, *b* and *c* in equation 2 are obtained correlating the measured oscillation periods to the known density of HFC-134, chosen as the calibration fluid. The equation proposed by [2] is used to determine the HFC-134a density at calibration pressure and temperature. The total uncertainty of this apparatus, estimated taking into account the influence of temperature, pressure, period of oscillations and HFC-134a EoS uncertainties, is around ± 0.1%. In order to check the accuracy of the vibrating tube densimeter technique, density measurements for HFC-152a (1,1-difluoroethane) and HFC-125 (pentafluoroethane) were carried out. Actually HFC-152a and HFC-125 were chosen because of the availability of accurate equations. Figures 3 and 4 show the deviations between the experimental data and the calculated data using the database REFPROP 6.0 [3] and, for HFC-152a, also using the equation proposed in [4]. In the present experimental temperature range, the deviations are within ± 0.1% for both fluids.
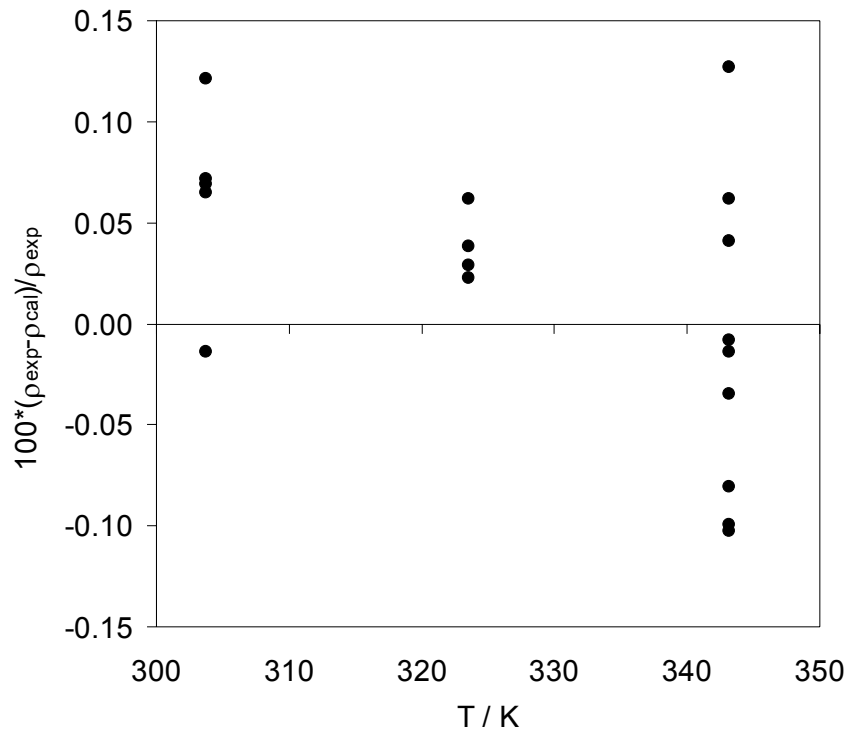
Figure3. Compressed liquid density deviations for HFC-125 with respect to REFPROP 6.0 [3].

2.2 Materials

HFC-134a and HFC-365mfc were provided by ICI and Solvay respectively and with a certified purity higher than 99.9% and 99.7% mol, respectively. Both products were used after several cycles of freezing with liquid nitrogen, evacuation, thawing and ultrasound. No impurities were detected by gas chromatography using both the flame ionization detector (FID) and the thermal conductivity detector (TCD).
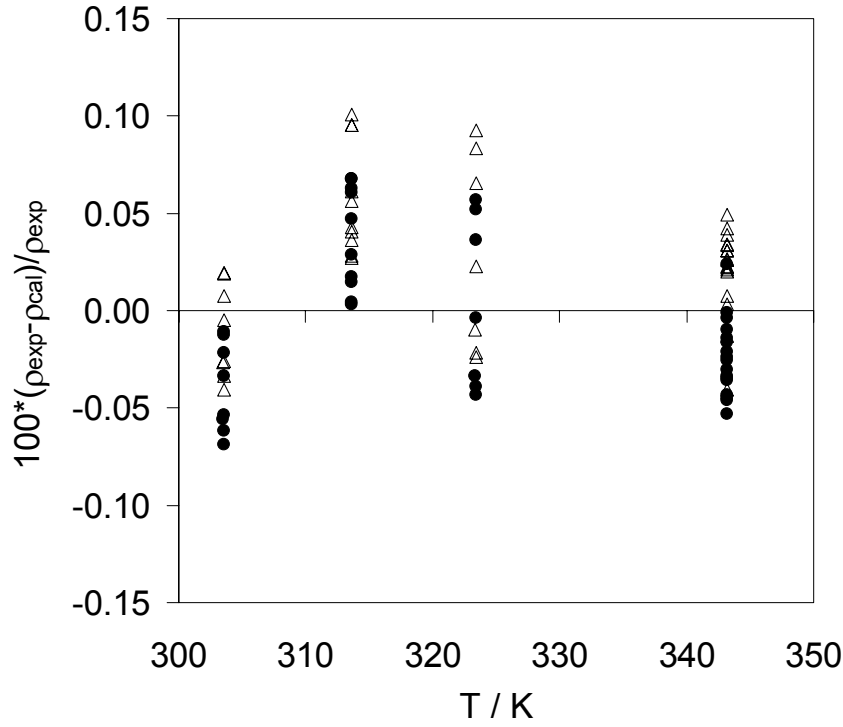
Figure 4. Compressed liquid density deviations for HFC-152a with respect to REFPROP 6.0 [3] (●) and [4] (Δ).

3. Results and discussion

3.1 Compressed liquid density

Compressed liquid density measurements were performed at pressure up to 25 MPa and at temperatures ranging from 283.15 to 343.15 K. A selection of these data are summarized in Table 1. Figure 5 shows their distribution on the (ρ, P) plane.

The obtained results were fitted to a generalized Tait equation in the form proposed by [5]:

$$v = v_{sat}\left(1 - c\,ln\frac{\beta + P}{\beta + P_{sat}}\right) \tag{3}$$

where v is the molar volume, v_{sat} is the saturated molar volume, P the pressure and P_{sat} the vapour pressure (determined from [6]) at a given temperature.

The terms β and c were obtained from the following equations:

$$\beta = P_c\left[-1 + a\left(1 - T_r\right)^{1/3} + b\left(1 - T_r\right)^{2/3} + d\left(1 - T_r\right) + e\left(1 - T_r\right)^{4/3}\right] \tag{4}$$

$$e = exp\left(f + g\omega + h\omega^2\right) \tag{5}$$

Table 1. Experimental compressed liquid density for the HFC-365mfc.

T (K)	P (kPa)	ρ (kg/m³)	T (K)	P (kPa)	ρ (kg/m³)	T (K)	P (kPa)	ρ (kg/m³)	T (K)	P (kPa)	ρ (kg/m³)
283.19	25012	1333.6	289.17	25088	1323.2	293.15	25005	1316.2	303.14	24921	1299.1
283.19	24007	1332.0	289.17	23003	1319.9	293.15	23016	1312.9	303.13	23078	1295.9
283.18	23000	1330.5	289.16	22028	1318.2	293.15	22012	1311.2	303.12	21048	1292.3
283.19	22050	1328.9	289.17	20947	1316.5	293.15	21042	1309.6	303.12	20098	1290.6
283.19	20013	1325.7	289.16	19002	1313.1	293.15	20039	1307.8	303.13	19075	1288.8
283.19	19009	1324.1	289.16	18008	1311.5	293.15	19059	1306.1	303.13	18021	1286.6
283.19	17903	1322.3	289.17	16993	1309.7	293.16	18006	1304.3	303.13	16974	1284.6
283.18	16027	1319.1	289.17	16026	1307.9	293.15	17028	1302.5	303.13	15985	1282.8
283.19	15001	1317.2	289.16	15065	1306.2	293.15	16021	1300.7	303.14	15051	1280.9
283.18	14006	1315.6	289.15	14017	1304.3	293.15	15002	1298.8	303.14	14057	1278.8
283.18	13004	1313.9	289.16	13065	1302.6	293.15	14014	1296.8	303.14	13040	1276.7
283.19	12017	1312.1	289.18	11998	1300.6	293.15	13003	1295.0	303.14	12010	1274.5
283.19	11004	1310.3	289.15	11011	1298.7	293.15	11965	1292.9	303.16	10992	1272.3
283.18	9990	1308.4	289.16	10004	1296.7	293.14	10111	1289.2	303.15	10037	1270.3
283.19	8061	1304.7	289.16	9002	1294.7	293.15	8938	1287.0	303.14	9058	1268.0
283.18	7040	1302.7	289.16	8000	1292.8	293.14	8064	1285.1	303.14	8039	1265.6
283.19	6011	1300.8	289.15	7067	1290.7	293.15	7012	1282.9	303.15	7007	1263.4
283.18	5002	1298.8	289.15	6060	1288.7	293.15	6004	1280.8	303.14	6003	1261.1
283.19	4070	1296.9	289.16	5038	1286.5	293.15	5015	1278.6	303.14	5018	1258.7
283.18	3047	1294.8	289.16	4022	1284.5	293.15	4005	1276.4	303.14	4002	1256.3
283.18	2009	1292.8	289.16	3005	1282.4	293.15	3017	1274.1	303.14	3004	1253.7
283.18	1013	1290.5	289.16	2002	1280.1	293.14	2057	1272.0	303.14	2009	1251.2
283.19	502	1289.4	289.15	1002	1277.8	293.14	1010	1269.5	303.15	1097	1248.9
283.18	276	1289.0	289.16	992	1277.8	293.15	512	1268.3	303.14	426	1247.1
283.19	120	1288.7	289.17	629	1277.0	293.15	459	1268.2	303.14	221	1246.5

T (K)	P (kPa)	ρ (kg/m³)	T (K)	P (kPa)	ρ (kg/m³)	T (K)	P (kPa)	ρ (kg/m³)	T (K)	P (kPa)	ρ (kg/m³)
313.15	25035	1282.2	323.14	25053	1263.6	333.15	25031	1246.8	343.15	25001	1226.8
313.15	23011	1278.3	323.15	23050	1259.8	333.16	23004	1242.4	343.15	23006	1222.3
313.16	22043	1276.4	323.15	21026	1255.6	333.16	22005	1240.2	343.15	21015	1217.6
313.16	21002	1274.4	323.15	19939	1253.4	333.16	21005	1237.9	343.15	20014	1215.2
313.16	20010	1272.5	323.15	19070	1251.5	333.16	20003	1235.6	343.15	19004	1212.7
313.15	19078	1270.5	323.14	18052	1249.5	333.17	19002	1233.2	343.15	18000	1210.1
313.15	18004	1268.4	323.15	17018	1247.1	333.17	18031	1230.9	343.15	17017	1207.4
313.16	17012	1266.1	323.15	16019	1244.8	333.16	17002	1228.4	343.15	16043	1204.7
313.15	16042	1264.1	323.15	15031	1242.4	333.16	16001	1225.8	343.15	15016	1201.9
313.15	15084	1262.1	323.15	14024	1240.0	333.16	15022	1223.2	343.15	14002	1198.9
313.15	14053	1259.8	323.15	13006	1237.5	333.16	13002	1218.0	343.16	13001	1196.0
313.15	13046	1257.5	323.15	12031	1235.1	333.16	12003	1215.1	343.15	12002	1193.0
313.15	12009	1255.1	323.16	11013	1232.5	333.16	10964	1212.1	343.15	10996	1189.7
313.16	11016	1252.8	323.16	10005	1229.9	333.16	10100	1209.6	343.15	9997	1186.5
313.16	10037	1250.5	323.15	9036	1227.4	333.16	9028	1206.4	343.15	9007	1183.2
313.15	9041	1247.9	323.15	8014	1224.6	333.15	8021	1203.2	343.15	8000	1179.7
313.15	8007	1245.4	323.14	7019	1221.6	333.16	7012	1200.1	343.14	7009	1176.2
313.16	7003	1242.9	323.15	5992	1218.6	333.16	6005	1196.8	343.15	6010	1172.4
313.16	6011	1240.3	323.15	5000	1215.7	333.17	5032	1193.5	343.15	5007	1168.6
313.15	5029	1237.6	323.16	4011	1212.6	333.16	4069	1190.2	343.15	4035	1164.8
313.16	4003	1234.9	323.16	3008	1209.6	333.16	3012	1186.4	343.15	3052	1160.7
313.16	3035	1232.1	323.16	2013	1206.4	333.17	2003	1182.7	343.15	1994	1156.3
313.16	2017	1229.3	323.15	1012	1202.9	333.17	1009	1178.9	343.15	999	1151.9
313.16	1005	1226.3	323.15	498	1201.2	333.16	853	1178.3	343.16	584	1150.0
313.15	555	1224.8	323.15	236	1200.4	333.17	631	1177.3	343.15	362	1149.0

$$c = j + k\omega \qquad (6)$$

Here ω is the acentric factor calculated through the basic equation:

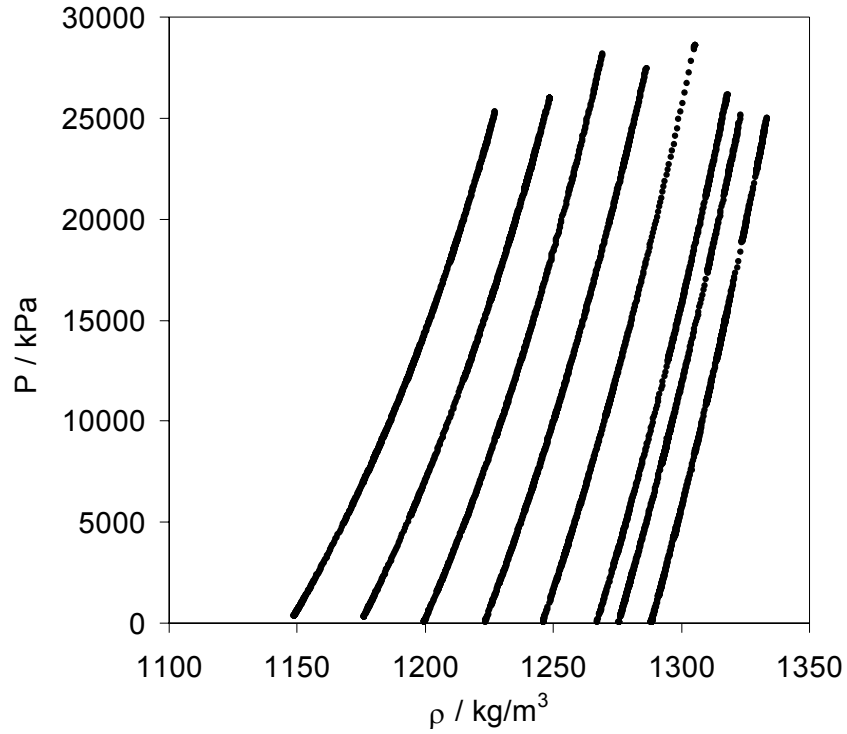$$\omega = -log_{10} P_{rsat(at\ T_r = 0.7)} - 1 = 0.233 \qquad (7)$$

where P_{rsat} is the reduced vapor pressure at the reduced temperature $T_r = 0.7$.

The following values of critical properties were used [6]:

$T_c = 477.7$ K

$P_c = 3489$ kPa

The a-k coefficients, regressed on the base of the experimental data, are given in Table 2. The deviations between equation 3 and the experimental data are reported in Figure 6.
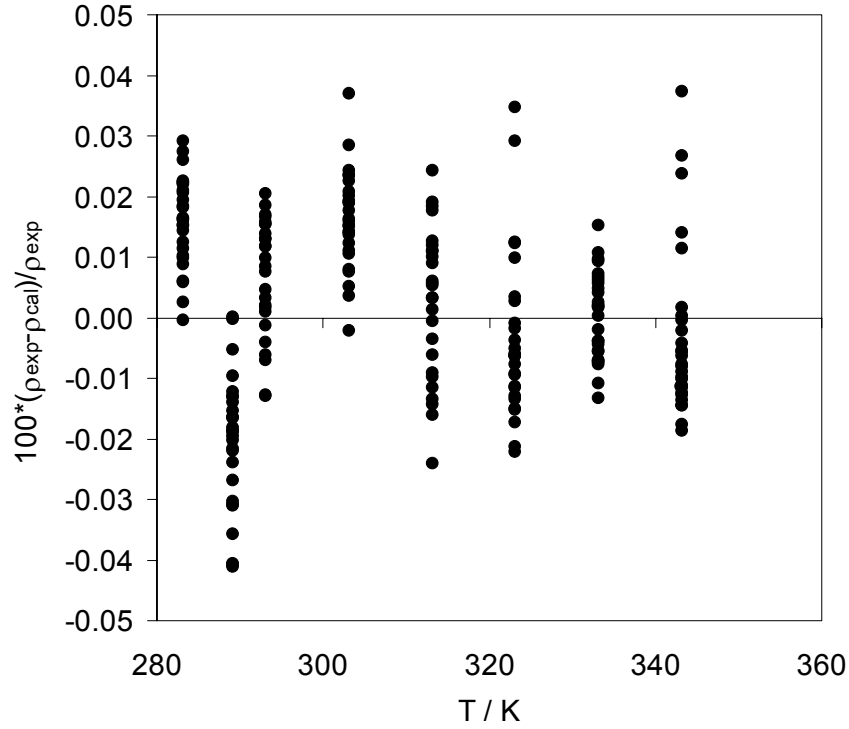

Figure 5. Distribution of the experimental density data.

Table 2. Coefficients of the generalised Tait equation for the HFC-365mfc.

Coefficient	Numerical value	Coefficient	Numerical value
a	75.05154	f	17.90495
b	-281.8640	g	-78.82263
c	-31.03131	h	-319.9452
d	277.2904	j	1.577197
e	140235	k	-6.457928

Figure 6. Deviations of the experimental density data for HFC-365mfc from the Tait equation (equation 3).

Our data have been compared with those from [6], which range between 289.15 K and 413.15 at a pressure up to 9.85 MPa. The declared uncertainty of these data is ± 0.2% on the measured density. The absolute average deviation between equation 3 and the data presented in the literature, is always within ±0.2% with a slight dependence on temperature. These deviations are reported in Figure 7.

3.2 Saturated liquid density

The saturated liquid density data (Figure 8) for HFC-365mfc were calculated extrapolating each isotherm at the vapour pressure using a third degree polynomial. HFC-365mfc vapour pressures were taken from [6]. The values of density at saturation are reported in Table 3. Then the saturated liquid density data (ρ_{sat} is in kg/m^3) were correlated with the following equation [7]:

$$\rho_{sat} = \rho_c \left(1 + A\tau^{1/3} + B\tau^{2/3} + C\tau + D\tau^{4/3}\right)$$ (8)

where:

$$\tau = 1 - \frac{T}{T_c}$$

and $\rho_c = 488$ kg/m^3 [6].

The parameters of equation 8 are reported in Table 4. The absolute average deviation between equation 8 and the extrapolated saturated liquid densities is ±0.1%. Saturation density data have been compared with literature data [6 8] and the deviations are reported in Figure 9. The deviations are within ± 0.2 % for the data of [6] and within ± 0.4 % for the data of [8].
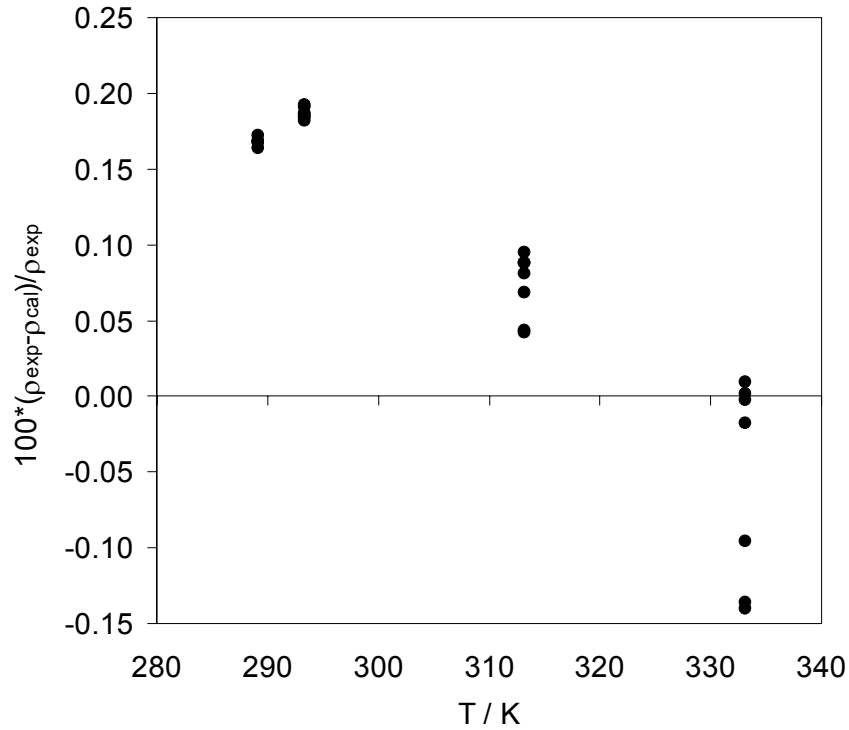

Figure 7. Deviations of the present experimental density data for HFC-365mfc from [6].

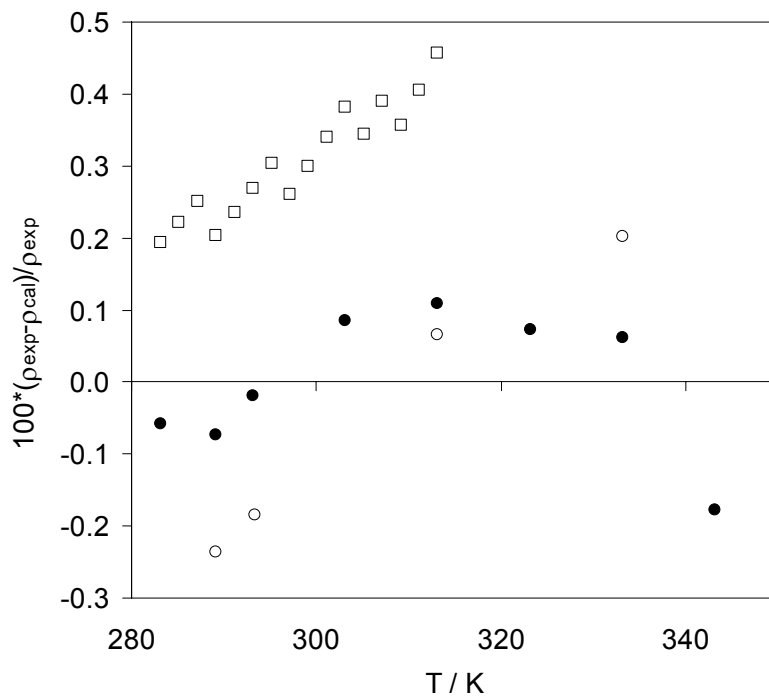**Table 3. Saturated liquid density data of HFC-365mfc.**

T (K)	P_{sat} (kPa)	ρ_{sat} (kg/m^3)	T (K)	P_{sat} (kPa)	ρ_{sat} (kg/m^3)
283.19	29.83	1288.7	313.15	100.55	1223.7
289.17	38.93	1275.4	323.14	142.23	1199.9
293.15	46.15	1267.4	333.15	196.54	1175.7
303.14	69.13	1246.3	343.15	265.65	1148.3

Table 4. Coefficients of equation 8.

A	B	C	D
1.11302	1.35275	0.03506	0.19825
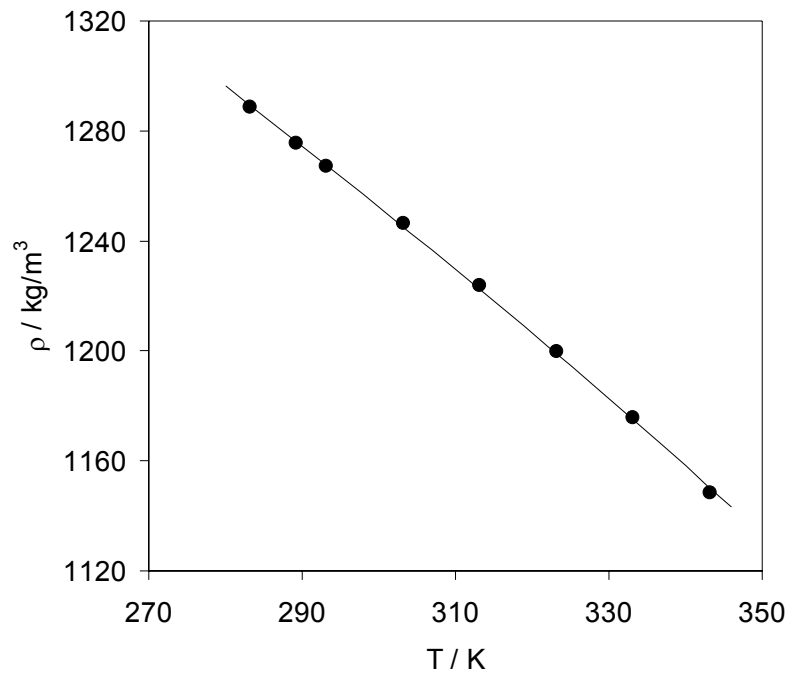
Figure 8. Distribution of the extrapolated saturation density data for HFC-365mfc (●) and data calculated from equation (8) (—).

Figure 9. Deviations of HFC-365mfc saturated density data from eq (8); this work (●), [6] (○) and [8] (□).

Conclusions

Compressed liquid density data for the 1,1,1,3,3-pentafluorobutane (HFC-365mfc) have been determined along 8 isotherms in the range between 283.15 K and 343.15 K. Our experimental data have been used to regress the parameters of a Tait equation. The average relative deviations between the model and the experimental results are within ±0.04%. A satisfactory agreement was found between the proposed correlation and the available literature data. The saturated liquid density has been calculated at the experimental temperatures by extrapolating the liquid density isotherms to the vapour pressures. The saturated liquid densities have been correlated with a four parameters equation in the reduced form. A good agreement has been found with the data of [6], while higher deviations appear with the data from [8].

List of symbol

P: pressure (kPa)
T: temperature (K)
P: pressure (kPa)
v: molar volume (m^3/mol)

Greek letters

π.   period of oscillation (μs)
ρ: liquid density (kg/m^3)

Subscripts

r: reduced property
sat: saturation property
c: critical constant

Acknowledgments

References

[1] S. Bobbo, L. Fedele, M. Scattolini, E. Camporese, J. Chem. Eng. Data 47-2, (2002) 179-182.

[2] R. Tillner-Roth., Int. J. Thermophys. 16-1 (1995) 91-100

[3] M. O. McLinden, S. S. Klein, E. J. Lemmon, A. P. G. Peskin, NIST Standard Reference Database 23, NIST Thermodynamic Properties of Refrigerants and Refrigerants Mixtures Database (REFPROP), Version 6.0 (1998) (Gaithersburg: National Institute of Standard and Technology).

[4] R. Tillner-Roth, H. D. Baher, J. Phys. Chem. Ref. Data 23-5 (1994) 657-729.

[5] G. Thomson, K. Brobst,R. Hankinson, J. Chem. Eng. Data 28 (1982) 671-676.

[6] M. Marrucho, N. S. Oliveira, R. Dohrn, J.Chem. Eng. Data 47 (2002) 554-558

[7] D. R. Defibaugh, G. Morrison, Fluid Phase Equilibria 80 (1992) 157-166.

[8] Solvay Fluor, private communication.